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(54) NONAQUEOUS ELECTROLYTIC BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To form a film on a positive electrode material at an interface with a nonaqueous electrolyte, and restrain reaction between the positive electrode material and the nonaqueous electrolyte by using a composite oxide of lithium transition metal containing at least Co and Mn as the positive electrode material, as well as a nonaqueous electrolyte composed of a solute containing at least one type of fluorine contained compound dissolved in a solvent which contains ethylene carbonate.

SOLUTION: A positive electrode material is made of a compound/ expressed by the formula of $\text{Li}_a\text{Co}_b\text{Mn}_c\text{MdNi}_1-(b+c+d)\text{O}_2$ where M stands for B, Al, Si, Ti, Fe, V, Cr, Cu, Zn, Ga and W, $0 < (a) < 1.2$, $0.1 \leq (b) < 1.0$, $0.05 \leq (c) < 1.0$, $0.05 \leq (d) < 1$, and $0.15 \leq (b+c+d) < 1$. A negative electrode is made of a carbonaceous material. Furthermore, a solvent is preferably prepared by mixing another solvent with ethylene carbonate, and LiPF_4 , LiBF_4 , $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ or the like is preferable as a fluoride compound for the solute of a nonaqueous electrolyte. As a result, a nonaqueous electrolytic battery with a high preservation characteristic and a high cycle characteristic can be provided.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] It is related with a nonaqueous electrolyte cell with nonaqueous electrolyte reacting in the nonaqueous electrolyte cell equipped with the positive electrode with which this invention used the lithium transition-metals multiple oxide for the positive-electrode ingredient, a negative electrode, and nonaqueous electrolyte with the positive-electrode ingredient in a positive electrode, and the negative-electrode ingredient in a negative electrode, and a preservation property and a cycle property falling [little].

[0002]

[Description of the Prior Art] In recent years, as one of the new style cells of high power and a high energy consistency, nonaqueous electrolyte is used for the electrolytic solution and oxidation of a lithium and the nonaqueous electrolyte cell of the high electromotive force using reduction came to be used.

[0003] Here, generally in such a nonaqueous electrolyte cell, the lithium transition-metals multiple oxide with which high tension is obtained comparatively was used as a positive-electrode ingredient in the positive electrode.

[0004] However, when such a lithium transition-metals multiple oxide was used for a positive-electrode ingredient, this positive-electrode ingredient and nonaqueous electrolyte reacted, nonaqueous electrolyte decomposed, and there was a problem that a preservation property and a cycle property worsened.

[0005] For this reason, in recent years, as shown in JP,4-184872,A, the mixed solvent of propylene carbonate and diethyl carbonate was used for the solvent in that nonaqueous electrolyte, and what controlled that above lithium transition-metals multiple oxides and nonaqueous electrolyte reacted was able to be considered.

[0006] However, when the lithium transition-metals multiple oxide containing transition metals, such as Co, nickel, and Mn, was used for a positive-electrode ingredient, in a charge condition, this positive-electrode ingredient still reacted with the above-mentioned nonaqueous electrolyte, and there was a problem that a charge preservation property worsened, especially.

[0007]

[Problem(s) to be Solved by the Invention] The positive electrode with which this invention used the lithium transition-metals multiple oxide for the positive-electrode ingredient, [when the lithium transition-metals multiple oxide which makes it a technical problem to solve the above problems in the nonaqueous electrolyte cell equipped with a negative electrode and nonaqueous electrolyte, and contains transition metals, such as Co, Mn, and nickel is used for a positive-electrode ingredient] Let it be a technical problem to obtain the nonaqueous electrolyte cell which it was fully controlled that this positive-electrode ingredient and nonaqueous electrolyte react, and was excellent in the preservation property or the cycle property.

[0008]

[Means for Solving the Problem] In the nonaqueous electrolyte cell in claim 1 of this invention In the nonaqueous electrolyte cell equipped with the positive electrode which used the lithium transition-metals multiple oxide for the positive-electrode ingredient, a negative electrode, and nonaqueous electrolyte in order to solve the above technical problems While using the lithium transition-metals multiple oxide which contains Co, and Mn and nickel in the above-mentioned positive-electrode ingredient at least, and using the solvent which contains ethylene carbonate in the above-mentioned nonaqueous electrolyte, the solute which contains a kind of fluorine-containing compound at least was used.

[0009] Like the nonaqueous electrolyte cell in this claim 1, and into a positive-electrode ingredient If the solute which contains a kind of fluorine-containing compound at least is used while using the lithium transition-metals multiple oxide which contains Co, and Mn and nickel at least, and using the solvent which contains ethylene carbonate in nonaqueous electrolyte In an interface with nonaqueous electrolyte, a coat comes to be formed in the above-mentioned positive-electrode ingredient, it is controlled that a positive-electrode ingredient and

nonaqueous electrolyte react also in a charge condition with this coat, and the preservation property and cycle property in a nonaqueous electrolyte cell improve.

[0010] In using for a positive-electrode ingredient the nickel transition-metals multiple oxide which contains Co, and Mn and nickel at least as mentioned above here, as this lithium transition-metals multiple oxide, as shown in claim 2 $\text{Li}_a\text{Co}_b\text{Mn}_c\text{M}_d\text{Ni}_{1-(b+c+d)}\text{O}_2$ (M is a kind of metal chosen from B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, and W at least) $0 < a < 1.2$ and $0.1 \leq b, 0.05 \leq c < 1, 0 \leq d < 1$, and $0.15 \leq b+c+d < 1$ are fulfilled. When it uses, a reaction with nonaqueous electrolyte is controlled more and a preservation property and a cycle property improve further.

[0011] Moreover, in the nonaqueous electrolyte cell in this invention, as a negative-electrode ingredient used for that negative electrode, although the well-known negative-electrode ingredient currently generally used conventionally can be used Especially, surface area is large like carbon materials, such as a graphite and corks, and it sets to what has high nonaqueous electrolyte and reactivity. By combining the above nonaqueous electrolyte, the reaction of this nonaqueous electrolyte and the carbon material which is a negative-electrode ingredient is also controlled, and a cycle property and a preservation property come to improve further.

[0012] Moreover, in the nonaqueous electrolyte cell in this invention, it is desirable to use it for it that what is necessary is just to use the solvent which contained ethylene carbonate at least as mentioned above as a solvent in that nonaqueous electrolyte, making this ethylene carbonate mix other well-known solvents.

[0013] If the ion conductivity in nonaqueous electrolyte will worsen if there are few amounts of this ethylene carbonate, and the amount of ethylene carbonate increases too much, since in making ethylene carbonate mix other solvents in this way the viscosity of nonaqueous electrolyte will become high and ion conductivity will fall also in this case here, it is desirable to make it the amount of the ethylene carbonate in a solvent become the range of 20 - 80vol% by the volume ratio.

[0014] The solute in the above-mentioned nonaqueous electrolyte that a kind of fluorine-containing compound should just be used above at least moreover, as this fluorine-containing compound The well-known fluorine-containing compound currently generally used as a solute can be used. for example, LiPF_6 , LiBF_4 , $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, and LiAsF_6 etc. -- it is also possible to be able to use it and to use it combining such a fluorine-containing compound and other well-known solutes.

[0015] Since the ion conductivity in nonaqueous electrolyte falls even if the amount of the solute which is added here in adding the solute which contains a kind of fluorine-containing compound in nonaqueous electrolyte at least increases too much and it decreases too much, it is made for the amount of the whole solute in nonaqueous electrolyte to become the range of 0.5 - 2.0 mol/l preferably.

[0016]

[Example] While lowering of the discharge capacity at the time of saving in the state of charge in the nonaqueous electrolyte cell of this example while giving the example and explaining the nonaqueous electrolyte cell of this invention concretely hereafter decreases, the example of a comparison is given and it is shown clearly that a cycle property improves. In addition, the nonaqueous electrolyte cell in this invention is not limited to what was shown in the following example, but in the range which does not change that summary, is changed suitably and can be carried out.

[0017] (Examples 1-8 and examples 1-3 of a comparison) In these examples, the cylindrical lithium secondary battery of AA size as shown in drawing 1 was produced using the positive electrode, the negative electrode, and nonaqueous electrolyte which were produced as follows.

[0018] In producing [production of positive electrode] positive electrode It is $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ as a positive-electrode ingredient. As opposed to this mixture after mixing this positive-electrode ingredient and the artificial graphite which is an electric conduction agent using powder The solution made to dissolve the polyvinylidene fluoride which is a binder in a N-methyl-2-pyrrolidone (NMP) is added. It kneaded so that a positive-electrode ingredient, an above-mentioned artificial graphite, and above-mentioned polyvinylidene fluoride might become the weight ratio of 85:10:5, and the slurry was prepared, this slurry was applied to both sides of the aluminium foil which is a positive-electrode charge collector with the doctor blade method, this was dried, and the positive electrode was produced.

[0019] In producing [production of negative electrode] negative electrode Spacing [in / as a negative-electrode ingredient / a lattice plane (002)] d002 This natural-graphite powder is received using the natural-graphite powder which is 3.35A. The solution made to dissolve the polyvinylidene fluoride which is a binder in above NMP is added. It kneaded so that the weight ratio of natural-graphite powder and polyvinylidene fluoride might be set to 95:5, and the slurry was prepared, this slurry was applied to both sides of the copper foil which is a negative-electrode charge collector with the doctor blade method, this was dried, and the negative electrode was produced.

[0020] As shown in the following table 1, while using ethylene carbonate for the solvent at least in examples 1-

7 in producing [production of nonaqueous electrolyte] nonaqueous electrolyte, a kind of fluorine-containing compound was used for the solute at least.

[0021] Here, it is LiPF₆ as a solute to the mixed solvent with which ethylene carbonate (EC) and diethyl carbonate (DEC) were mixed by the volume ratio of 50:50 in the example 1. It is made to dissolve at a rate of 1 mol/l. It sets in the example 2 and is LiBF₄ as a solute to the same mixed solvent as an example 1. It is made to dissolve at a rate of 1 mol/l. It sets in the example 3 and is LiN (C₂ F₅ SO₂)₂ as a solute to the same mixed solvent as an example 1. It is made to dissolve at a rate of 1 mol/l. It sets in the example 4 and is LiAsF₆ as a solute to the same mixed solvent as an example 1. It is made to dissolve at a rate of 1 mol/l. It is LiPF₆ as a solute to the mixed solvent with which EC and dimethyl carbonate (DMC) were mixed by the volume ratio of 50:50 in the example 5. It is made to dissolve at a rate of 1 mol/l. It is LiPF₆ to the mixed solvent with which EC and gamma-butyrolactone (G-BL) were mixed by the volume ratio of 50:50 in the example 6. It is made to dissolve at a rate of 1 mol/l. It sets in the example 7 and is LiPF₆ to the same mixed solvent as an example 1. LiClO₄ It is made to dissolve at a rate of 0.5 mol/l, respectively. It is LiPF₆ to the mixed solvent with which EC, and propylene carbonate (PC) and DEC were mixed by the volume ratio of 25:25:50 in the example 8. It was made to dissolve at a rate of 1 mol/l, and each nonaqueous electrolyte was produced.

[0022] On the other hand, it sets for the example 1 of a comparison, and is LiClO₄ as a solute to the same mixed solvent of EC and DEC as an example 1. It is made to dissolve at a rate of 1 mol/l. It is LiPF₆ to the mixed solvent with which DEC was mixed by the volume ratio of PC and 50:50 in the example 2 of a comparison. It is made to dissolve at a rate of 1 mol/l. It is LiPF₆ to the mixed solvent with which PC and 1 and 2-dimethoxyethane (DME) were mixed by the volume ratio of 1:1 in the example 3 of a comparison. It was made to dissolve at a rate of 1 mol/l, and each nonaqueous electrolyte was produced.

[0023] In producing [production of cell] cell As shown in drawing 1, between the positive electrodes 1 and negative electrodes 2 which were produced as mentioned above After having made the fine porous membrane of lithium ion permeability intervene as a separator 3, rolling these in the shape of a spiral and making it hold in the cell can 4, Pour in each nonaqueous electrolyte produced as mentioned above in this cell can 4, respectively, and it is obturated. While connecting the positive electrode 1 to the positive-electrode external terminal 6 through the positive-electrode lead 5, the negative electrode 2 was connected to the cell can 4 through the negative-electrode lead 7, and the insulating packing 8 was made to separate electrically the positive-electrode external terminal 6 and the cell can 4.

[0024] next, about each lithium secondary battery of the examples 1-8 produced as mentioned above and the examples 1-3 of a comparison After making it charge to charge termination electrical-potential-difference 4.2V by 200mA of charging currents, respectively, Discharge to discharge-final-voltage 2.75V by 200mA of discharge currents, and the discharge capacity in each lithium secondary battery before preservation is measured. Then, each above-mentioned lithium secondary battery is made to charge to charge termination electrical-potential-difference 4.2V by 200mA of charging currents, respectively. Thus, after saving each charged lithium secondary battery for 20 days under a 60-degree C ambient atmosphere, each lithium secondary battery is returned to a room temperature. While discharging to discharge-final-voltage 2.75V by 200mA of discharge currents, respectively and measuring the discharge capacity after preservation, the capacity survival rate after preservation was searched for, and these results were shown according to the following table 1.

[0025]

[A table 1]

正極材料: $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$					
	混合溶媒 (体積比)	溶質の種類	放電容量(mAh)		容量 残存率 (%)
			保存前	保存後	
実施例 1	EC:DEC =50:50	LiPF_6	6 0 0	5 1 5	85.8
実施例 2	EC:DEC =50:50	LiBF_4	5 9 5	5 0 5	84.9
実施例 3	EC:DEC =50:50	$\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$	6 0 0	5 1 0	85.0
実施例 4	EC:DEC =50:50	LiAsF_6	5 8 0	4 7 0	81.0
実施例 5	EC:DMC =50:50	LiPF_6	6 0 0	5 1 0	85.0
実施例 6	EC:G-BL=50:50	LiPF_6	5 9 0	5 0 0	84.7
実施例 7	EC:DEC =50:50	$\text{LiPF}_6+\text{LiClO}_4$	5 8 0	4 6 5	80.2
実施例 8	EC:PC:DEC =25:25:50	LiPF_6	5 8 5	4 9 5	84.6
比較例 1	EC:DEC =50:50	LiClO_4	5 8 0	3 9 5	68.1
比較例 2	PC:DEC =50:50	LiPF_6	5 0 0	2 7 0	54.0
比較例 3	PC:DME =50:50	LiPF_6	5 0 0	2 5 0	50.0

[0026] [when nickel and the lithium transition-metals multiple oxide containing Co and Mn are used for a positive electrode so that clearly from this result] Each lithium secondary battery of the examples 1-8 which used the solute which contains a fluorine-containing compound in a solute while using the solvent which contains ethylene carbonate in the solvent of nonaqueous electrolyte The lithium secondary battery of the example 1 of a comparison which does not contain a fluorine-containing compound in the solute in nonaqueous electrolyte, It compared with the lithium secondary battery of the examples 2 and 3 of a comparison which do not contain ethylene carbonate in the solvent in nonaqueous electrolyte, and there was little lowering of the discharge capacity after saving all, and the capacity survival rate was improving remarkably.

[0027] moreover, example 1- which used only the fluorine-containing compound for the solute in nonaqueous electrolyte when the lithium secondary battery of the above-mentioned examples 1-8 was compared -- each lithium secondary battery of 6 and 8 Compared with the lithium secondary battery of the example 7 which added a fluorine-containing compound and solutes other than this, and lowering of the discharge capacity after preservation has decreased. Especially, they are LiPF_6 , LiBF_4 , and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ to a solute. Each used lithium secondary battery is LiAsF_6 to a solute. It compared with the used lithium secondary battery of an example 4, and lowering of the discharge capacity after preservation had decreased further.

[0028] In these examples and the example of a comparison (Examples 9-17 and examples 4-9 of a comparison) Only the positive-electrode ingredient used for the case of the lithium secondary battery of the above-mentioned example 1 and a positive electrode is made to change. It is LiPF_6 to the mixed solvent with which the negative-electrode ingredient in a negative electrode was made to mix DEC by the volume ratio of EC and 50:50 to nonaqueous electrolyte, using the above-mentioned natural graphite. What was dissolved at a rate of 1 mol/l is used. Each lithium secondary battery was produced respectively like the case of the above-mentioned example 1.

[0029] Here, in these examples and the example of a comparison, as shown in the following table 2 as the positive-electrode ingredient, that from which Li, nickel, and Co and Mn became the rate shown in this table is used, and that in which at least one of nickel, and the Co(es) and Mn is not contained was used in the thing of the examples 4-9 of a comparison.

[0030] And also about each lithium secondary battery of the examples 9-17 produced using such a positive-electrode ingredient, and the examples 4-9 of a comparison, like the above-mentioned case, while measuring the discharge capacity before preservation, and the discharge capacity after preservation, the capacity survival rate after preservation was searched for, and these results were shown according to the following table 2.

[0031]

[A table 2]

	正極材料				放電容量 (mA h)		容量残存率 (%)
	Li	Ni	Co	Mn	保存前	保存後	
実施例9	1	0.85	0.1	0.05	605	515	85.1
実施例10	1	0.5	0.45	0.05	600	510	85.0
実施例11	1	0.5	0.1	0.4	590	500	84.7
実施例12	1	0.6	0.2	0.2	600	510	85.0
実施例13	1	0.5	0.3	0.2	595	505	84.9
実施例14	1	0.4	0.4	0.2	580	465	80.2
実施例15	1	0.05	0.1	0.85	580	460	79.3
実施例16	1	0.05	0.9	0.05	580	460	79.3
実施例17	1	0.9	0.05	0.05	600	390	65.0
比較例4	1	1	0	0	620	375	60.5
比較例5	1	0	1	0	580	360	62.0
比較例6	1	0	0	1	530	300	56.6
比較例7	1	0.9	0.1	0	610	375	61.5
比較例8	1	0	0.9	0.1	570	365	64.0
比較例9	1	0.1	0	0.9	545	320	58.7

[0032] [when the nonaqueous electrolyte which dissolved the solute containing a fluorine-containing compound in the solvent containing ethylene carbonate is used so that clearly from this result] Each lithium secondary battery of the examples 9-17 which used the lithium transition-metals multiple oxide which contains nickel, and Co and Mn in the positive-electrode ingredient in the positive electrode It compared with each lithium secondary battery of the examples 4-9 of a comparison which used nickel, and any of Co and Mn or the lithium transition-metals multiple oxide with which one or more are not contained for the positive-electrode ingredient, and there was little lowering of the discharge capacity after saving all, and the capacity survival rate was improving.

[0033] Moreover, when the lithium secondary battery of the above-mentioned examples 9-17 is compared, Positive-electrode ingredient $\text{Li}_a\text{Co}_b\text{Mn}_c\text{Md}$ nickel $1-(b+c+d)$ O_2 shown in aforementioned claim 2 (M is a kind of metal chosen from B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, and W at least) $0 < a < 1.2$ and $0.1 \leq --$ the conditions of $b < 1$, $0.05 \leq c < 1$, $0 \leq d < 1$, and $0.15 \leq b+c+d < 1$ are fulfilled. it is -- each lithium secondary battery of the examples 9-16 which used the positive-electrode ingredient with which M was not contained but d was set to 0 It compared with the lithium secondary battery of the example 17 which used the positive-electrode ingredient which does not fulfill this condition, lowering of the discharge capacity after preservation decreased further, and the capacity survival rate was improving remarkably.

[0034] Only the positive-electrode ingredient used for the case of the lithium secondary battery of the above-mentioned example 1 and a positive electrode is made to change also in these examples. (Examples 18-28) It is LiPF_6 to the mixed solvent with which the negative-electrode ingredient in a negative electrode was made to mix DEC by the volume ratio of EC and 50:50 to nonaqueous electrolyte, using the above-mentioned natural graphite. What was dissolved at a rate of 1 mol/l is used. Each lithium secondary battery was produced respectively like the case of the above-mentioned example 1.

[0035] Here, it sets for these examples and the example of a comparison, and is $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.1}\text{M}_{0.1}\text{O}_2$ as that positive-electrode ingredient. It is shown by the formula and the thing which made the class of metal of M in this formula change as shown in the following table 3 was used.

[0036] And also about each lithium secondary battery of the examples 18-28 produced using such a positive-electrode ingredient, like the above-mentioned case, while measuring the discharge capacity before preservation, and the discharge capacity after preservation, the capacity survival rate after preservation was searched for, and these results were shown according to the following table 3.

[0037]

[A table 3]

正極材料 : $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{M}_{0.1}\text{O}_2$				
	Mの種類	放電容量 (mAh)		容量残存率 (%)
		保存前	保存後	
実施例 18	B	595	485	81.5
実施例 19	Al	580	465	80.2
実施例 20	Si	595	480	80.7
実施例 21	Ti	590	480	81.4
実施例 22	Fe	590	475	80.5
実施例 23	V	590	475	80.5
実施例 24	Cr	590	470	79.7
実施例 25	Cu	595	475	79.8
実施例 26	Zn	585	475	81.2
実施例 27	Ga	585	470	80.3
実施例 28	W	585	475	81.2

[0038] So that clearly from this result like each lithium secondary battery of examples 18-28 [when the lithium transition-metals multiple oxide containing the metal shown in a positive-electrode ingredient by the above-mentioned M besides nickel, and Co and Mn is used] When the nonaqueous electrolyte which dissolved the solute containing a fluorine-containing compound in the solvent containing ethylene carbonate was used, it compared with the lithium secondary battery of each aforementioned example of a comparison, lowering of the discharge capacity after preservation decreased, and the capacity survival rate was improving remarkably.

[0039] Next, it sets under a 60-degree C ambient atmosphere, respectively about each lithium secondary battery of the above-mentioned examples 1-16, examples 18-28, and the examples 2 and 3 of a comparison. After making it charge to charge termination electrical-potential-difference 4.2V by 200mA of charging currents, it discharges to discharge-final-voltage 2.75V by 200mA of discharge currents. It carried out by having repeated charge and discharge by making this into 1 cycle, the relation of the number of cycles and discharge capacity in each lithium secondary battery was investigated, and the result was shown in drawing 2.

[0040] Consequently, compared with each lithium secondary battery of the examples 2 and 3 of a comparison, the lowering of the discharge capacity accompanying the increment in the number of cycles of each lithium secondary battery of the above-mentioned examples 1-16 and examples 18-28 has decreased, and the cycle property in a lithium secondary battery was improving.

[0041]

[Effect of the Invention] In a nonaqueous electrolyte cell [in / as explained in full detail above / claim 1 of this invention] While using the lithium transition-metals multiple oxide which contains Co, and Mn and nickel in a positive-electrode ingredient at least Since the nonaqueous electrolyte which dissolved the solute which contains a kind of fluorine-containing compound at least in the solvent containing ethylene carbonate was used, In the interface with nonaqueous electrolyte, the coat was formed in the above-mentioned positive-electrode ingredient, it was controlled that a positive-electrode ingredient and nonaqueous electrolyte react also in a charge condition with this coat, and the preservation property and cycle property in a nonaqueous electrolyte cell improved remarkably.

[0042] Moreover, $\text{Li}_a\text{Co}_b\text{Mn}_c\text{Md}_{1-(b+c+d)}\text{O}_2$ shown in claim 2 as a lithium transition-metals multiple oxide (M is a kind of metal chosen from B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, and W at least) $0 < a < 1.2$ and $0.1 \leq b+c+d < 1$ are fulfilled. When it was used for a positive-electrode ingredient, more, the reaction with nonaqueous electrolyte was controlled and the preservation property and cycle property in a nonaqueous electrolyte cell improved further.